

# Photodissociation of phenylacetylene at 193 nm: Observation of two primary channels using photofragment translational spectroscopy

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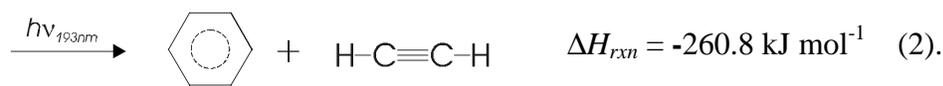
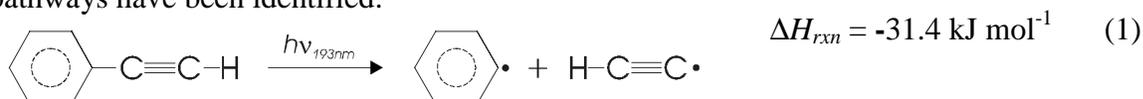
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## INTRODUCTION

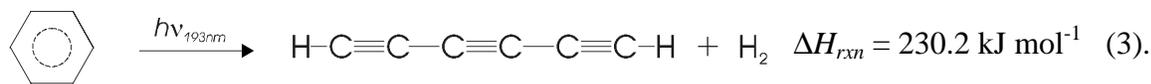
Phenylacetylene (PA) is an aromatic molecule with an unsaturated side group and is commonly used as a precursor for the synthesis of the polymer polyphenylacetylene  $[(-RCCH)_n]$ , where R = phenyl]. The polymer is stable in air, soluble in most organic solvents, and has many interesting properties such as non-linear optical properties<sup>1</sup> and its potential use in semiconductor, electrophotographic photoreceptor, and chemical sensor devices.<sup>2-4</sup>

Poly-PA is commonly synthesized using a variety of catalytic methods with PA as the starting material. The catalysts used in these syntheses include Ziegler-Natta-type catalysts, transition metal halides and carbonyls, ionic catalysts, and free radicals.<sup>5-9</sup> Recently, photo-induced catalysis of poly-PA has been investigated as an alternative approach to the traditional methods mentioned above.<sup>10-16</sup> For molecules such as PA which absorb strongly in the ultraviolet, the photochemical initiation of polymerization is an efficient process. Surprisingly little is known about the photochemistry of PA. Knowledge of the primary photochemical processes is critical in the control and design of polymerization processes involving PA.

Several vibronic bands of PA have been observed in the UV and are attributed to excitation of the ring electrons with vibrational coupling to the C-C stretch of the acetylenic moiety.<sup>17-18</sup> We have carried out an investigation of the photodissociation of PA at 193 nm to gain more insight into the primary processes involved. At 193 nm, the vibronic transitions have been assigned to the excitation of the  $A^1A_1 \rightarrow D^1A_1$  or  $A^1A_1 \rightarrow E^1A_1$  systems.<sup>17</sup> Two primary photochemical pathways have been identified:



Serendipitously, the UV photochemistry of PA is simple. Reaction (1) produces the free radicals – ethynyl and phenyl, while reaction (2) gives way to two closed shell molecules – benzyne and acetylene. The amount of energy released in reaction (2) is sufficient to induce a secondary reaction:



Only the internally excited benzyne molecules undergo dissociation. From the energetic threshold for reaction (3), we derived an enthalpy of formation of  $669 \pm 14 \text{ kJ mol}^{-1}$  for 1,3,5-hexatri-yne.

## EXPERIMENTAL SECTION

All experiments were conducted at beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam machine which has been described in detail elsewhere.<sup>11</sup> Helium was bubbled through a furan sample held at  $-21$  °C. At this temperature and a total pressure of 800 Torr, a 10% molecular beam of furan/He was generated. This mixture was fed through pulsed valve (General Valve) and expanded from a nozzle heated to  $\sim 100$ °C in a differentially pumped source region and into the main chamber.

The photolysis laser was an ArF excimer (193.3 nm, Lambda Physik LPX 220i), focused to a spot of size 2x4 mm and aligned perpendicular to the plane containing the molecular beam and detector axis, on the axis of rotation of the molecular beam source. Photofragments entering the triply differentially pumped detector region ( $9 \times 10^{-11}$  Torr) were photoionized 15.2 cm from the interaction region using tunable synchrotron radiation. The characteristics of the light source are discussed in detail elsewhere, but include an intensity of  $10^{16}$  photons/sec (quasi-continuous), an energy bandwidth of 2.2%, and a cross section in the probe region of 0.2x0.1 mm. The tunability of the light source allows for selective ionization of products and very low background counts. The photoionized products were mass selected by using a quadrupole mass filter and the ions were

counted with a Daly ion counter.<sup>12</sup>

Time-of-flight of the products were measured with a multichannel scalar (EG&G Ortec Turbo MCS).

The bin width for the MCS was fixed at 0.75 or 1  $\mu$ sec for the measurements reported here. Timing sequences for the laser, pulsed valve, and the MCS were maintained by a digital delay generator (Stanford Research Systems, Inc. Model 535). Furan (99%) was obtained from Aldrich and used without further purification.

## RESULTS

Signal was observed for m/e 25, 26, 24, 76, and 77. Due to lack of space, however, we will show data for only reactions (2) and (3). Photo-ion efficiency measurements for m/e 76 and 74 allowed us to identify these fragments as benzyne and 1,3,5-hexyne, respectively.

The measured time-of-flight (TOF) spectra for reaction (2) is shown in the Figs. 1 and 2. These figures also show the fit to the data using the forward convolution technique. The

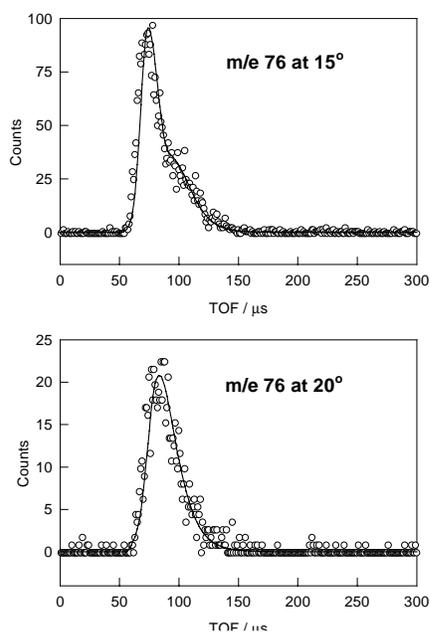


Figure 2. TOF spectra for m/e 76 ( $C_6H_4$ ) at  $15^\circ$  and  $20^\circ$  laboratory angles.

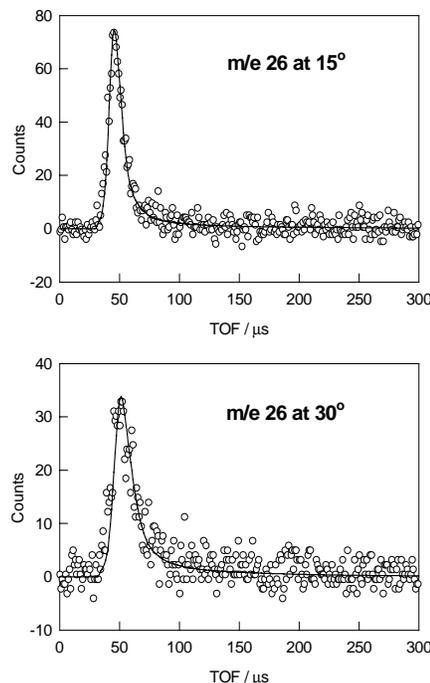


Figure 1. TOF spectra for m/e 26 ( $C_2H_2$ ) at  $15^\circ$  and  $30^\circ$  laboratory angles.

resulting center-of-mass translational energy distributions  $[P(E)]$  are shown in Fig. 3. For reaction (2), the fit for  $m/e$  26 gave a  $P(E)$  with an average translational energy,  $\langle E_T \rangle$ , of 12.09 kcal/mol. Using this distribution, we were unable to fit the slow part of the  $m/e$  76 TOF. The slow fragments in turn have more internal energy. The data suggests that these fragments (i.e benzyne molecules with internal excitation) were undergoing secondary dissociation [i.e. reaction (3)]. In fact, from the difference between the  $m/e$  26 and  $m/e$  76 center of mass translational energy distributions, one can derive the  $\Delta H_{rxn}$  for reaction (3). Figure 3 shows the difference for these distributions. Note the sharp cutoff in the resulting  $P(E)$ . This cutoff is the energetic threshold for the secondary dissociation of benzyne and from which we have derived  $\Delta H_f = 669 \pm 14 \text{ kJ mol}^{-1}$  for 1,3,5-hexatriene.

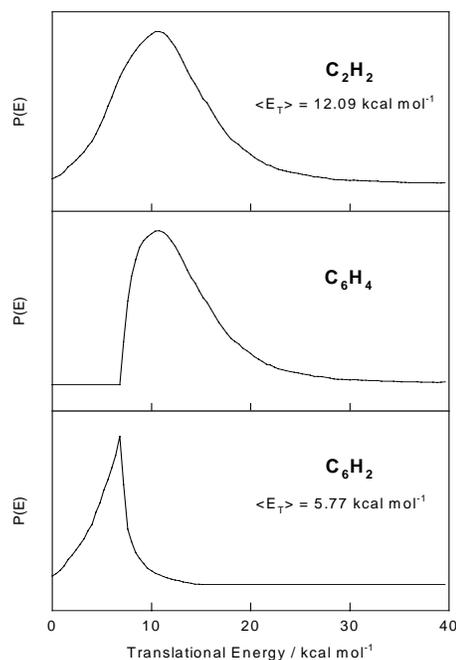


Figure 3. Center of mass translational energy distributions for reactions (2) and (3). Refer to text for further explanation.

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